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(54) Constant potential electrochemical gas sensor

(57) The sensor comprises a gas-permeable membrane 20 and an oxygen permeable membrane 36 at opposite ends of a housing, an electrolyte filled reaction chamber P, a work electrode 21 which is always in contact with the electrolyte, and counter and reference electrodes 23, 24. The electrodes are connected to a potentiostat. The gas permeable membrane 20 is independent from the work electrode 21 and both are laid of a water-permeable, porous member 22 whose projection 22a extends into the electrolyte P, thus wetting the work electrode 21 with electrolyte P by capillary attraction. The sensor may be used to detect carbon monoxide, hydrogen sulphide, ozone or gases used in manufacturing semiconductors.

FIG. 3

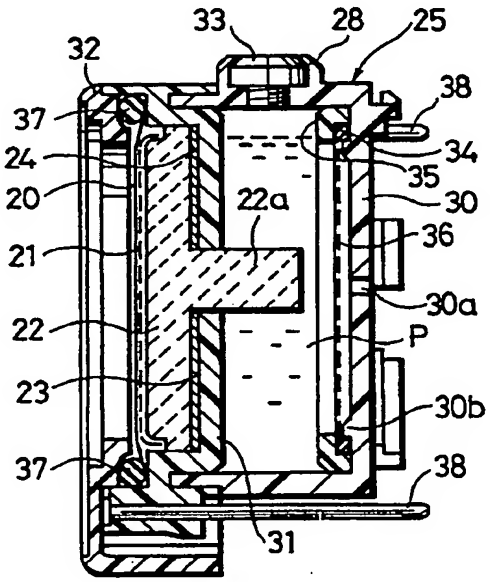

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FIG. 1

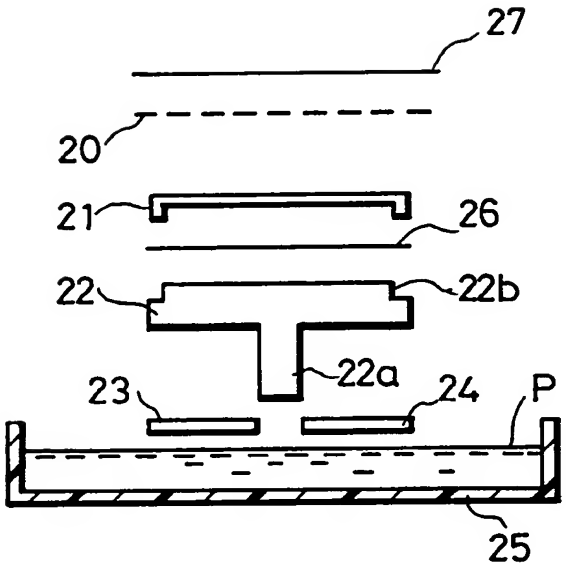


FIG. 2

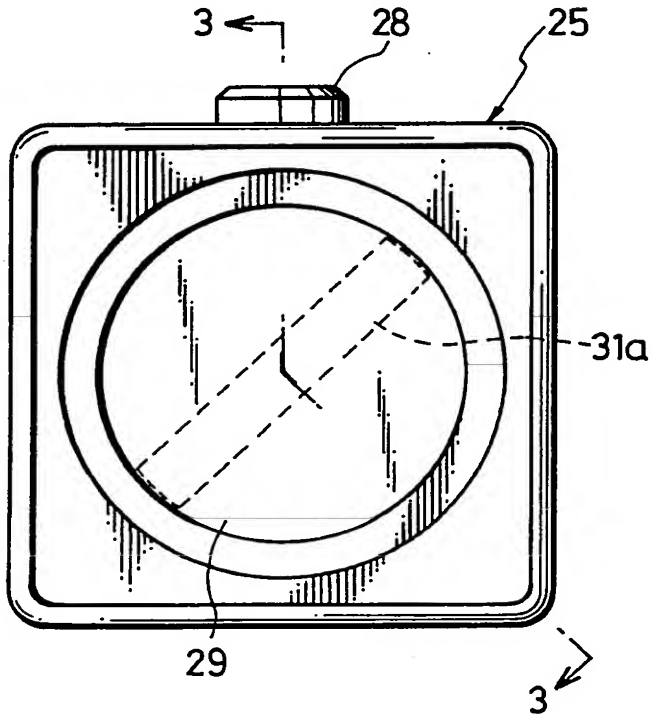


FIG. 3

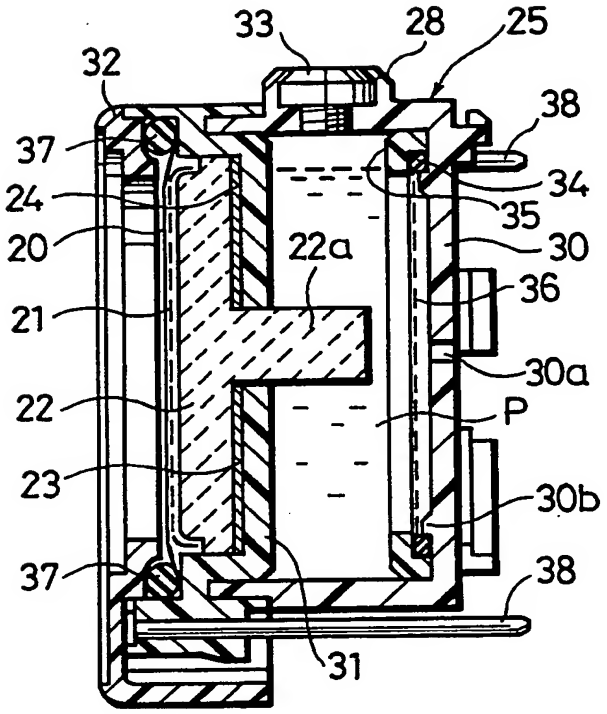
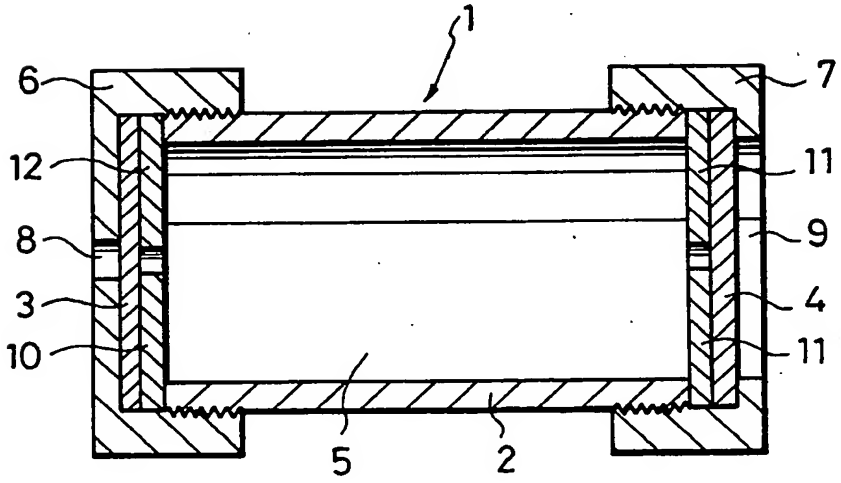


FIG. 4 PRIOR ART



Constant potential electrolytic gas sensor

The present invention relates to constant potential electrolytic gas sensors which are used in quantitative detection of different gasses such as carbon monoxide, hydrogen sulfide, ozone or gasses used in manufacturing semiconductors.

Some dangerous gasses which may have an injurious effect on human beings, animals and plants, or inflammable or explosive gasses are used in living circumstances. Such dangerous gasses may be leaked in factories or working sites. Carbon monoxide or hydrogen sulfide of high concentration may cause fatal accidents. Gas sensors using the constant potential electrolytic method are used to detect and determine the concentration of such gas with accuracy.

One example of such a constant potential electrolytic gas sensor is disclosed in Japanese Patent 55-87943(A), and is shown in Fig.4. It comprises a casing 1 having a hollow cylinder 2, an oxygen-permeable membrane 3 of polymer resin fixed to one end of the hollow cylinder 2 and a gas-permeable membrane 4 of polymer resin fixed to the other end of the hollow cylinder 2, thus defining a closed reaction cell, which is filled with an electrolyte.

Specifically, the oxygen-permeable membrane 3 and the gas-permeable membrane 4 are fixed to the opposite ends of the hollow cylinder 2 by covers 6 and 7, whose tapped insides are screwed into the opposite threaded ends of the hollow cylinder 2. The cover 6 has an oxygen inlet aperture 8 at its center whereas the cover 7 has a gas inlet opening 9. The oxygen-permeable membrane 3 has a counter electrode 10 and a reference electrode 12 on its inner surface whereas the gas-permeable membrane 4 has a work electrode 11 connected to its inner surface via a catalyst. The integration of gas-permeable membrane 4 and catalyst of a noble metal such as palladium or platinum when being put in contact with a gas to be detected will permit

the catalyst to expedite the decomposing of the gas passing through the membrane, supplying electrons and hydrogen ions into the electrolyte. On the other hand the oxygen of the surrounding air after passing through the oxygen-permeable membrane 3 flows into the electrolyte in the vicinity of the counter electrode 10. Thus, the cathode reaction will be caused when such oxygen meets with electrons and hydrogen ions supplied from the work electrode, and then, such reaction is converted into electricity, and the gas is detected in terms of the quantity of so converted electricity.

The membrane-and-catalyst integration is made by: applying Teflon (R.T.M) resin adhesive to a polymer resin gas-permeable membrane; applying a noble metal catalyst layer to the gas-permeable membrane; and heating the laminated structure to form an integration. The heating causes the closing of minute holes of the polymer resin membrane, thereby locally changing the permeability of the gas-permeable membrane. Thus, the gas-permeable membrane is liable to have uneven permeability over its whole area, locally losing gas-permeability in the membrane. As a result the conversion to electricity and the quickness in response are not satisfactory as presumed.

The work and other electrodes contact directly with electrolyte, and therefore, the three-phase interfaces (contact areas) between the catalyst of the work electrode, the gas-permeable membrane and the electrolyte are liable to be affected by deformation of the membrane, the surrounding temperature and humidity and other physical factors with the result that the sensitivity of the sensor varies with time. As a matter of fact the condition in which the work and other electrodes contact with the electrolyte varies greatly by changing the posture of the sensor in use, for instance by inclining the sensor in measurement. Thus the sensitivity of the sensor depends on what posture the sensor may take.

One object of the present invention is to provide a constant

potential electrolytic gas sensor whose sensitivity is guaranteed free of the lowering of sensitivity with time under affection of the surrounding temperature and humidity and without causing an adverse effect on the permeability or other desired functions of gas-permeable membrane.

Another object of the present invention is to provide a constant potential electrolytic gas sensor whose sensitivity is independent of what posture the sensor may take in measurement.

To attain these objects a constant potential electrolytic gas sensor comprising a casing defining a reaction cell filled with an electrolyte, a gas-permeable membrane fixed between the reaction cell and the gas inlet on one side of the casing, an oxygen-permeable membrane fixed between the reaction cell and the oxygen inlet on the other side of the casing, a work electrode to work on a gas to be detected, said work electrode being put in contact with the electrolyte all the time, a counter electrode to supply oxygen, a reference electrode to permit constant potential measurement, and electricity collecting terminals each connected to these electrodes at one end and to selected potentiostuds of an associated gauge, is improved according to the present invention in that said gas-permeable membrane is independent and separate from said work electrode.

An ordinary gas-permeable membrane of polymer resin is used. As described above, the conventional gas-permeable membrane is made by preparing a lamination of a polymer resin membrane, a noble metal catalyst layer and a work electrode, and subjecting the lamination to the heating treatment to form an integration. In this connection polymer resins other than Teflon can be seldom used. Thanks to the gas-permeable membrane being independent and separate from the work electrode, the liberty of selecting materials in designing is increased. Thus, polymer resins other than Teflon can be used. Also, advantageously the nature or structure of the selected gas-permeable membrane can be fully used for the purpose without causing an adverse effect on the

permeability of the membrane.

A work electrode may be made by fixing a noble catalyst such as palladium or platinum to a metal gauze or an electrically conductive perforated object and by subjecting the catalyst bearing perforated object to thermal treatment. It is not necessary to use gas-permeable membrane as fixing means, and therefore the liberty of selecting materials for fixing means is increased, and electrically conductive materials can be selected, thereby facilitating necessary electric connections to the work electrode. Also, advantageously the electric resistance at the work electrode is stable, thereby assuring that the electric output provided by the gas reaction, the quickness in response and other prescribed functions remain stable with time.

In such a gas sensor the gas after passing through the gas-permeable membrane comes to contact with the work electrode, causing electrons and hydrogen ions to be released into the electrolyte. The cathode reaction is caused when these electrons and hydrogen ions come to meet with oxygen, which is supplied from the counter electrode after oxygen of the surrounding air is permitted to pass through the oxygen-permeable membrane. The electric current caused by the cathode reaction is allowed to flow to the potentiostuds of an associated gauge through the current collection terminals, thus permitting the detecting of the gas concentration in terms of electric current. It should be noted that the oxygen-permeable membrane functions to control the pressure prevailing in the reaction cell.

A water-permeable porous member is placed between the electrolyte and the gas-permeable membrane-and-work electrode combination. The counter electrode and the reference electrode are applied to the water-permeable porous member on the side on which the gas-permeable membrane-and-work electrode combination is applied. The water-permeable porous member causes the capillary attraction on electrolyte to draw it toward the work electrode and the counter and reference electrodes, thereby wet-

ting these electrodes with electrolyte all the time. Such a water-permeable porous member may be made of a hard inorganic substance such as ceramics. Nonwoven fabric or filter paper may be used, but inadvantageously these materials will swell to change their volumes. This intervening porous matter has the effect of making the gas sensor insensitive to surrounding temperature, humidity and other circumferential factors, thereby improving the accuracy with which the gas sensor can determine the gas concentration.

The water-permeable porous member may have a projection extending in the reaction cell with its axial end close to the other end of the casing and with its radial ends close to the circumference of the casing, thus assuring that the water-permeable porous member is kept in contact with the electrolyte all the time no matter what posture the gas sensor may take. Also, the casing may have an apertured partition between the water-permeable porous member and the reaction cell, permitting the projection of the porous member to pass through the aperture of the apertured partition. The counter and reference electrodes are positioned on the opposite sides of the projection of the porous member, sandwiched between the apertured partition and the porous member. This arrangement has the effect of assuring the accuracy in measurement no matter what posture the gas sensor may take. The projection of the water-permeable porous member may have an inclined plate-like shape or a cylindrical or post-like shape.

Other objects and advantages of the present invention will be understood from the following description of a constant potential electrolytic gas sensor according to a preferred embodiment of the present invention, which is shown in accompanying drawings.

Fig.1 shows the positional relationship in which parts and elements are to be assembled to a constant potential electrolytic gas sensor according to the present invention;

Fig.2 is a front view of the constant potential electrolytic gas sensor;
Fig.3 is a section taken along the line 3-3 in Fig.2; and
Fig.4 is a section of a conventional constant potential electrolytic gas sensor.

Referring to Fig.1, the main parts of a constant potential electrolytic gas sensor according to the present invention are shown in an exploded fashion to indicate how these parts are positioned and assembled to form the gas sensor. Specifically they are a gas-permeable membrane 20, a work electrode 21, a water-permeable porous member 22, a counter electrode 23 and a reference electrode 24.

The water-permeable porous member 22 is made of ceramics, and it is a circular disk having a rectangular projection 22a across its diameter, and therefore it has a "T"-shape in section. It is fitted in the casing of the sensor with its projection 22a extending in the reaction cell of the casing. As seen from Fig.1, the circular disk has a circumferential, stepwise notch 22b on the front side which is opposite to the rear side on which the projection 22a is formed.

The work electrode 21 is laid on the front side of the water-permeable porous member 22, and the gas-permeable membrane of polymer resin 20 is laid on the work electrode 21. On the other hand, the counter electrode 23 and the reference electrode 24 are laid on the rear side of the water-permeable porous member 22 to sandwich the projection 22a between these electrodes 23 and 24. The assembly is fitted in the casing 25 as later described.

The work electrode 21 is made by fixing a noble catalyst to a stainless steel gauze (150 mesh) and by subjecting the catalyst-and-wire gauze integration to thermal treatment. As seen from Fig.1, the circular circumference of the wire gauze is bent to fit on the circumferentially notched rear surface of the water-

permeable porous member 22. A glass fiber filter 26 is laid between the work electrode 21 and the water-permeable porous member 22.

The gas-permeable membrane 20 is made of fluororesin, and a filter 27 is made of perforated stainless steel coated with Teflon. The filter 27 is laid between the gas-permeable membrane 20 and the casing 25 as reinforcement. The counter and reference electrodes 23 and 24 are semicircular in shape, and are made of stainless steel gauze as is the case with the work electrode 21. The work electrode 21 may be a perforated stainless steel foil, which can be made by making pores in a stainless steel foil at selected positions by etching.

Referring to Fig.2, the casing 25 has a liquid inlet 28 on its ceiling and a center gas inlet 29 on its front side. Fig.3 is a sectional view of Fig.2 taken along the 45-degree bent line 3-3 and viewed in the direction indicated by arrows, thus permitting the corner structure of the gas sensor to be shown in the lower half of the drawing. As shown, the casing 25 includes a rear tank 30, an electrode holder 31 and a front cover 32. The rear tank 30 has a rectangular box-like shape, opening on its front side, and the plate-like electrode holder 31 is fitted in the opening of the rear tank 30 to define a reaction cell. A front cover 32 is fitted on the opening circumference of the electrode holder 31.

The electrolyte inlet 28 is formed on the ceiling of the rear tank 30, and is closed by screwing an associated plug 33. The reaction cell is defined by the electrode holder 31 in the rear tank 30, and is filled with electrolyte P. The rear tank 30 has an oxygen inlet 30a on its rear side. The inside circumference of the rear tank 30 has an annular ridge 30b, and a ring guide 35 is applied to the rear tank 30 to hold the Tefron (trademark) oxygen supply/pressure control membrane 36 with an O-ring 34 hermetically applied therearound.

As seen from Fig.2, the plate-like electrode holder 31 has a rectangular hole 31a inclined at the angle of 45 degrees, thereby permitting the projection 22a of the water-permeable, porous member 22 to pass through the plate-like electrode holder 31. As seen from Fig.3, the water-permeable, porous member 22 is assembled with the plate-like electrode holder 31 by inserting the projection 22a of the porous member 22 in the rectangular hole 31a of the electrode holder 31, thus sandwiching the semicircular counter and reference electrodes 23 and 24 between the porous member 22 and the electrode holder 31, and allowing the projection 22a to extend into the electrolyte P in the reaction cell.

The annular front cover 32 has a detection opening 29, and it is fitted on the opening end of the electrode holder 31 to apply the glass fiber filter 26, the work electrode 21, the gas-permeable membrane 20 and the filter 27 to the water-permeable porous member 22 in the order named when viewed in the inside-to-outside direction. Specifically the glass fiber filter 26 is laid on the water-permeable, porous member 22 with its circumference fitted in the circumferential notch 22b of the porous member 22; the work electrode 21 is laid on the glass fiber filter 26; the gas-permeable membrane 20 is laid on the work electrode 21; and finally the filter 27 is laid on the gas-permeable membrane 20. The lamination is held by the annular front cover 32 using an O-ring 37 to hermetically seal the circumference of the lamination.

The casing 25 has current-collection rods 38 fixed to its corners, extending rearward to permit detachable connection to an associated gas gauge.

In use the electrolyte will penetrate into the projection 22a of the water-permeable porous member 22 to reach the counter and reference electrodes 23 and 24 and the work electrode 21, thus wetting these electrodes all the time. Although the work electrode 21 can be wetted with electrolyte under the influence

of capillary attraction, the use of the glass fiber filter 26 assures the wetting of the whole area of the work electrode 21 with electrolyte.

The liquid-, gas- and solid-phase interfaces between these different electrodes 21, 23 and 24, the gas-permeable membrane 20 and the electrolyte P are defined positively by the porous solid body 22, which cannot be changed in shape and size. Thus, these parts are pressed at a fixed pressure all the time, being independent from the surrounding temperature and humidity.

The stableness in the three-phase interfaces as described above and the positive dipping of electrolyte carrier in the electrolyte assure the constant supply of electrolyte to the three-phase interfaces of the gas sensor no matter what posture the gas sensor may take. Thus, the measurement accuracy is guaranteed free of variations for any measuring postures.

As is apparent from the above, the advantages provided by the constant potential electrolytic gas sensor structure according to the present invention are:

Construction of the gas-permeable membrane and the work electrode as separate parts increases the liberty with which the material and structure of the gas-permeable membrane can be selected, making full use of the characteristics of the selected material and structure in designing without deteriorating the performance of gas permission and separation, and obviating the necessity of using the gas-permeable membrane as catalyst holding means at the work electrode, and hence permitting the use of electrically conductive materials to facilitate the electric connection from the work electrode to the exterior. The electric resistance at the electrode remains unchanged, thus causing no adverse effects on the prescribed electric output, quickness in response and other prescribed performances with the result that the precise measurement is assured.

The three-phase interfaces are defined positively by the porous solid body, which cannot be changed in shape and size. Thus, the associated parts are pressed at a fixed pressure all the time, being independent from the surrounding temperature and humidity.

The positive dipping of electrolyte carrier in the electrolyte assures the constant supply of electrolyte to the three-phase interfaces of the gas sensor no matter what posture the gas sensor may take. Thus, the measurement accuracy is guaranteed free of variations for any measuring postures.

Claims:

1. A constant potential electrolytic gas sensor comprising a casing defining a reaction cell filled with an electrolyte, a gas-permeable membrane fixed between the reaction cell and the gas inlet on one side of the casing, an oxygen-permeable membrane fixed between the reaction cell and the oxygen inlet on the other side of the casing, a work electrode to work on a gas to be detected, said work electrode being put in contact with the electrolyte all the time, a counter electrode to supply oxygen, a reference electrode to permit constant potential measurement, and electricity collecting terminals each connected to these electrodes at one end and to selected potentiostuds of an associated gauge, characterized in that said gas-permeable membrane is independent and separate from said work electrode.

2. A constant potential electrolytic gas sensor according to Claim 1, wherein it further comprises a water-permeable porous member intervening between said gas-permeable membrane and work electrode and said electrolyte.

3. A constant potential electrolytic gas sensor according to Claim 2, wherein said water-permeable porous member has a projection extending in said reaction cell with its axial end close to the other end of said casing and its radial ends close to the circumference of said casing, thus assuring that said water-permeable porous member contacts the electrolyte all the time no matter what posture the gas sensor may take.

4. A constant potential electrolytic gas sensor according to Claim 3, wherein said casing has an apertured partition between said water-permeable porous member and said reaction cell, permitting said projection to pass through the aperture of said apertured partition, and positioning said counter electrode and said reference electrode on the opposite sides of said projection of said water-permeable porous member, sandwiched between said apertured partition and said water-permeable porous member.

5. A constant potential electrolytic gas sensor according to Claim 2, wherein said water-permeable porous member is made of ceramics.

6. A constant potential electrolytic gas sensor, substantially as described herein with reference to Figs. 1-3 of the drawings.

Patents Act 1977
Examiner's report to the Comptroller under Section 17
(The Search report)

Application number
GB 9405358.4

Relevant Technical Fields

(i) UK Cl (Ed.M) G1N (NBMS, NBMT, NBPMX, NBPX)

(ii) Int Cl (Ed.5) G01N (27/49)

Search Examiner
D MOBBS

Date of completion of Search
9 JUNE 1994

Databases (see below)
(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASE: WPI

Documents considered relevant following a search in respect of Claims :-
1-6

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
Y	GB 2164156 A	(MINE SAFETY APPLIANCES)	1-3
Y	EP 0084935 A1	(HITACHI)	1-3
Y	US 3755125	(ENVIROMETRICS) see particularly Figure 11 and column 4 line 50 to column 5 line 55	1-3

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).